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MONONITRATION OF DURENE

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(NASA-TM-77774) MONONITRATION OF DURENE
(National Aeronautics and Space
Administration) 19 p NC AC2/MF A01 CSCL 07D

N85-14892

Unclas
63/25 11020

Translation of "Das Problem der Mononitrierung von
DuroI", Helvetica Chimica Acta, Vol. 52 (6), No. 158,
1969, pp 1537-1548.



STANDARD TITLE PAGE

1. Report No. TM 77774	2. Government Accession No.	3. Recipient's Catalog No.	
4. Title and Subtitle MONONITRATION OF DURENE		5. Report Date December 1984	
		6. Performing Organization Code	
7. Author(s) Hanna, S.B.; Hunziker, E., Saito, T; Zollinger, H.		8. Performing Organization Report No.	
		10. Work Unit No.	
9. Performing Organization Name and Address Leo Kanner Associates, Redwood City, CA 94063		11. Contract or Grant No. NASW-4005	
		12. Type of Report and Period Covered Translation	
12. Sponsoring Agency Name and Address National Aeronautics and Space Administration Washington, D.C. 20546		14. Sponsoring Agency Code	
15. Supplementary Notes : Translation of "Das Problem der Mononitrierung von Duro1", : Helvetica Chimica Acta, Vol. 52 (6), No. 158, 1969, pp 1537-1548.			
16. Abstract In contrast to previous investigations, reaction conditions were found under which the nitration of durene gave predominantly, and in high yield, mononitrodurene (I), rather than dinitrodurene. The nitrating agent was $\text{NO}_2^+ \text{PF}_6^-$. Nitration with nitrosulfuric acid also gave mononitrodurene; however, by-products such as 2,3,5,6- $\text{Me}_4\text{C}_6\text{HCH}_2\text{C}_6\text{H}_2\text{Me}_3$ -2,4,5, were also formed. $\text{NO}_2^+ \text{PF}_6^-$ gave an intermediate additional compound with durene. The reaction carried out with 3,6-dideuterodurene in D_2O showed no isotope effect.			
17. Key Words (Selected by Author(s))		18. Distribution Statement Unlimited-Unclassified	
19. Security Classif. (of this report) Unclassified	20. Security Classif. (of this page) Unclassified	21. No. of Pages 17	22.

MONONITRATION OF DURENE

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(June 24th, 1969)

Summary

In contrast to many previous investigations, reaction conditions were found under which the nitration of durene (nitrating ratio 1:1) gives predominantly, and in high yield, mononitrodurene rather than the usually formed dinitrodurene (plus unreacted durene). The method consists in nitrating by nitryl phosphorohexafluoride in nitromethane as solvent in the presence of two equivalents of water.

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With mixed acids ($\text{HNO}_3 + \text{H}_2\text{SO}_4$) in nitromethane and in acetonitrile durene forms also mono- but no dinitrodurene; but under most conditions by-products are formed. Some of the by-products were identified.

Some preliminary mechanistic results are reported: An additional complex of unknown structure is rapidly formed; 3,6-dideuterodurene + D_2O do not show a hydrogen isotope effect; the preferential formation of dinitrodurene under conventional conditions is due to the fact that the reaction occurs at encounter-controlled rate.

1. Problem Situation.

Already during the 19th century several research workers pointed out the peculiar observation that durene (i.e., 1,2,4,5-tetramethylbenzol) produces, when nitrated, only dinitro-durene but no mononitrodurene [1]. In addition Neef [2] and Francis [3] observed that under certain conditions durene had a distinct tendency toward nitration of side-chains.

Willstätter & Kubli [4], who were able to confirm the results of previous workers, assumed that the dinitro-product formed not via the mononitro-compound but via an unstable, additional product of nitric acid.

* Numbers in the margin indicate pagination in the foreign text.

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More recently, G. & M.P. Illuminati [5] have worked with nitration of durene by means of nitric acid in a sulfuric-chloroform mixture according to Smith [6]. Under such conditions about four times as much dinitrodurene as mononitro-compounds are formed on the condition that the original products are used in a stoichiometric relationship of 1:1. A corresponding amount of non-reacted durene should, thus, be regenerated under these circumstances. In contrast to Willstätter & Kubli [4] the latter authors as well as Fuson [7] assumed that mononitrodurene was actually formed but reacted to a further stage more rapidly than durene. Fuson saw the reason for this as due to the heterogenous system and assumed that mononitrodurene was more easily dissolved than durene during the actual nitration phase of the system.

The experimental observations concerning the nitration of durene are fundamentally contrary to our general knowledge of the mechanism of electrophilic substitution and the effect of the reactivity of benzol derivatives via substitutes: accordingly, a nitro-radical should be able to reduce the further electrophilic substitution of the benzol ring by a factor of $>10^4$. On the other hand, it seems of interest to us to use the nitration method with nitrylic salts in organic, aprotic, polar solvents according to Olah [8] in the case of durene in order to, in that manner, arrive at a preparative method for producing mononitrodurene. Finally, such an investigation was important to us from a mechanistic point of view in connection with our previous work concerning the nitration of pentamethylbenzol [9]. /1538

2. Nitration of Durene by Means of Nitrylphosphorohexafluoride in Nitromethane

2.1 Nitration in Agitator Flasks

Since our research on the nitration of pentamethylbenzol [9] had demonstrated that tetramethyl sulfone (sulfolan) is very hygroscopic and, consequently, leads to uncertain results, we used nitromethane as solvent; solutions of both compounds were mixed and the reaction was halted by means of water after the time indicated in Table 1. Following the addition of a small amount of naphthalin in the form of a gaschromatographic standard, the mixture of products was analyzed by means of gaschromatography.

TABLE 1. NITRATION EXPERIMENTS IN NITROMETHANE IN AN AGITATOR FLASK AT $30^{\circ}\pm 1^{\circ}\text{C}$.

Test no.	Conc. of educts (mol/l)		Reaction time (min)	Products (mol%) ¹			
	durene	$\text{NO}_2^+\text{PF}_6^-$		durene	MND	DND	by-products
1a	0.034	0.034	45	41.9	5.9	40.9	11.3
1b	0.034	0.034	180	36.2	6.7	42.1	15.0
2a	0.031	0.031	4	50.3	4.8	44.9	-
2b	0.031	0.031	110	42.5	4.9	43.8	8.8
3	0.190	0.190	2	48.7	4.8	46.5	-

¹ MND and DND, respectively = mono-, dinitro-durene. The mol% of the by-product was estimated on the basis of the nitrocompounds, the durene regenerated and the standard (i.e., naphthalin).

The reaction is very fast; in spite of the fact that it takes place during the homogenous phase and that the components are added in a stoichiometric relationship of 1:1, eight to ten times as much dinitrodurene as mononitrodurene is formed (Table 1).

Under similar conditions as in Table 1, but while using tetramethylene sulfone as solvent, about 50% by-products are formed; this corresponds to the experience gained from nitration of pentamethylbenzol [9].

2.2 Nitration in Rapidly Mixing Flow Systems

When using a mixing apparatus according to Gordon & Wahl [10], the relationship of the reaction products, i.e., dinitrodurene (DND) and mononitrodurene (MND), changes in favor of the MND compound in comparison with the experiments made while using an ordinary agitator flask (Fig. 1). In addition, it happens that the relation of DND to MND depends on the concentration of educts: in relation to increasing dilution, this relationship approaches 0 (Fig.1).

These experiment demonstrate experimentally that the assumption made by Fuson [7] was correct: since the nitrylic salts are strongly electrophilic reagents, the reaction will under conventional mixing conditions occur

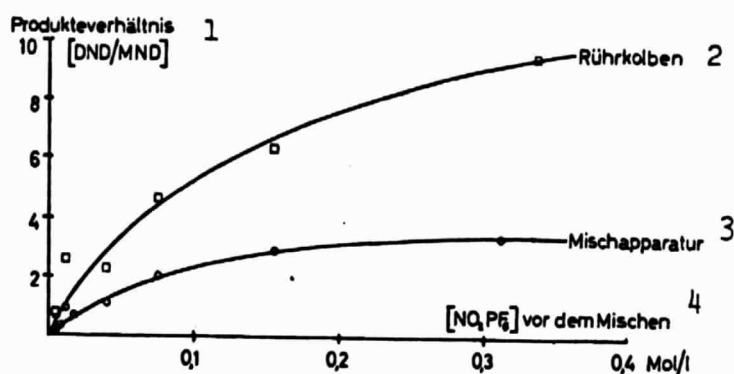


Fig. 1. Relationship between the products, i.e., DND and MND, during nitration of durene by means of nitrylphosphorohexafluoride in nitromethane.

- Key: 1. Relationship between products (DND/MND).
 2. Agitator flask.
 3. Mixing apparatus.
 4. $[\text{NO}_2\text{PF}_6]$ before mixing.

instantly at the surface bordering on the nitrylic salt solution. The relationship between the products is, thus, determined by an encounter-controlled phenomenon. It is, furthermore, impossible to draw any conclusions concerning relative velocity constants from competitive reactionary tests made under conventional reaction conditions².

3. The Effect of Water on the Nitration of Durene by Means of Nitrylphosphorohexafluoride in Nitromethane and Acetonitrile

It turned out that durene together with an equivalent amount of nitrylic salt in nitromethane furnished a large amount of MND but only minimum amounts of DND if, before the reaction, 2 equivalents of water are added (Table 2).

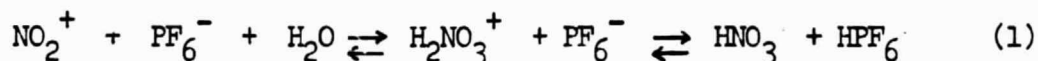
The water was added before the reaction of the solution of nitrylic salt in the corresponding solvent. Thereby, the equilibrium (1) appears to be infinitely displaced toward the right hand side. We can only preliminarily deduce on the basis of the conclusions below that under our conditions the equilibrium is displaced practically all the way to the right hand side, i.e., so that the nitryl ion occurs only in an infinitesimal concentration or that the nitric acid molecule acts as a weakly electrophilic (and, thus, more selec-

² In this connection we refer to the interpretation of competitive experiments with nitrylic salt nitration made by Tolgyesi [11].

TABLE 2. NITRATION OF DURENE IN THE PRESENCE OF 2 EQUIVALENT PARTS OF WATER IN ORGANIC SOLVENTS.

Test No.	Solvent	Conc. of educts (mol/l)			Temp. °C	Reaction time (min)	Products (mol%)				by-products
		durene	$\text{NO}_2^+ \text{PO}_6^-$	H_2O			durene	MND	DND		
4	CH_3NO_2	0.0053	0.0053	0.0106	20±0.5	18	11.4	78.9	-		9.7
5	CH_3NO_2	0.039	0.039	0.070	30±1	11	10.6	81.0	2.0		6.4
6	CH_3NO_2	0.248	0.248	0.480	30±1	10	7.1	68.9	2.0		22.0
7	CH_3CN	0.020	0.020	0.040	20±0.5	42	8.4	78.0	-		13.7

tive) nitration medium:



1. The experiments, described in section 4.1 and using mixed acids, resulted, similarly, in MND and no DND under conditions where, apparently, nitryl ions are still present. We are, thus, not yet able to solve the problem, whether the nitryl ion, the nitric acid molecule or a third kind of electrophilic reagent is the one, attacking the durene molecule during the tests described in that section.

2. In Fig. 2, the time-related dependency of the disappearance of durene and the formation of MND and by-products is illustrated. It can be seen that the reaction does not follow any simple kinetic laws. The S-shaped graphs of the concentrations of durene and of MND could, formally, be associated with an autocatalytic reaction. A similar observation was made by Schofield [12] during nitration of anthracene in 7.5% aqueous sulfonal.

During the nitration of durene by means of solutions of nitrylic salt and water in acetonitrile (Table 2, test no. 7), the solution turned rapidly dark brown; by time, this color gradually disappeared. It is evident from the UV spectra that, temporarily, an absorption band appears with a maximum at 340 nm. In Fig. 3, the extinction at this wavelength is illustrated as a function of time. /1541

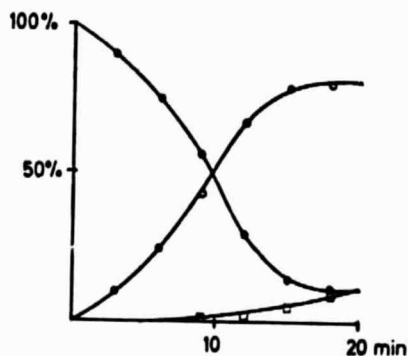


Fig. 2. Gaschromatographic analysis of the durene nitration test no. 4 (Table 2):
● durene; ○ MND; □ by-products.

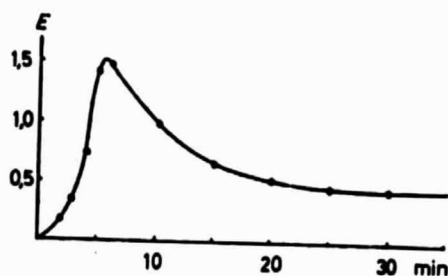


Fig. 3. Time-dependency of the absorption band at 340 nm in a system of durene/ $\text{NO}_2\text{PF}_6/\text{H}_2\text{O}$ in acetonitrile.

Since we assume that this absorption band can be considered representative of an intermediary product of the durene nitration and that its disappearance is catalyzed by the water, we tested the behavior of 3,6-dideutero-durene and heavy water under similar conditions. However, the alteration of the extinction at 340 nm occurred during this experiment in the same manner as during the normal arrangement. It is, thus, not likely that the water molecule functions as a proton acceptor for the aromatic hydrogen to be substituted during the velocity-determining phase.

In order to interpret the prevalent appearance of DND and the small yield of MND during the earlier tests (1 - 7), we have taken the feasibility of a formation of a special, additional product into consideration, i.e., one, from which DND can develop directly without using MND as an intermediary step. The following experiments, which were performed in addition, speak against such an explanation, which was for the first time discussed by Willstätter & Kubli [4].

1. On the basis of competitive nitration of mesitylene together with durene or MND in a Gordon & Wahl [10] apparatus, it turned out that the capacity for reaction of durene as well as of MND is practically equal on the condition that the reactivity of durene is statistically corrected by the presence of 2 equivalent, reactive positions (Table 3). From this follows that, if not a very thorough mixing of the reactive components is assured, the nitrating reagent will react again in its immediate vicinity following the primary nitration (i.e., the formation of MND) and, thus, the same molecule

/1542

TABLE 3. COMPETITIVE NITRATION OF MESITYLENE, DURENE, MND
PENTAMETHYLBENZOL IN NITROMETHANE.

Test No.	Molar relation of the educts ¹	Initial conc. of NO ₂ PF ₆ (mol/l)	Temp. °C	Reaction time (s)	Products	Molar relationships ¹ Educts reacted with nitryl salt	DND/MND products
M 1	Mesitylene 11.4 Durene 10.4 NO ₂ PF ₆ 1	0.0319	20°	0.54	Mesitylene 1 MNM 0.0325 DNM 0.0028 Durene 0.9719 MDN 0.0258 DND 0.0052	Mesitylene = $\frac{1}{0.950}$	DNM/MNM = 0.086 DND/MNM = 0.202
M 2	Mesitylene 13.6 MND 13.7 NO ₂ PF ₆ 1	0.0268	20°	0.54	Mesitylene 1 MNM 0.0379 DNM 0.0034 MND 1.0507 DND 0.0210	Mesitylene = $\frac{1}{0.470}$	DNM/MNM = 0.090
M 3	Mesitylene 10.7 PMB 10.0 HMB 0.6 NO ₂ PF ₆ 1	0.0351	20°	0.54	Mesitylene 1 MNM 0.0365 DNM 0.0041 PMB 0.980 NO ₂ PMB 0.0337 HMB 0.0616	Mesitylene = $\frac{1}{0.754}$	DNM/MNM = 0.112

¹ PMB = pentamethylbenzol; HMB = hexamethylbenzol (a contaminant in PMB); MNM and DNM = mono- and dinitromesitylene. Example for calculating the relationships in the 7th column (Test no. M 1):
(325) + 56) / (258 + 104) = 1/0.950.

will a second time be attacked with a velocity not essentially lesser than that of durene.³ In other words, it can be assumed that the attack of the nitrating reagent on durene and on MND is encounter-controlled.

2. Under the conditions used by us for the nitration experiments, no criteria were obtained from the measurements of the conductivity of nitrylic

³ The fact that the nitro-radical of MND has no strongly deactivating effect during a dual nitration is actually not surprising, since the co-polarity of the first nitro-radical is strongly impeded by the adjacent methyl radical.

salt in nitromethane, which indicated any triplet or quadruplet ions: in Figs. 4 and 5 the specific and the molar conductivity of nitryl phosphorohexafluoride in nitromethane are illustrated in relation to increasing concentration. Should /1543 it be feasible to demonstrate that these are associates with two nitryl ions per associate, it could be assumed that, in such a complex, DND could develop directly from that kind of an aggregate plus one molecule of durene.

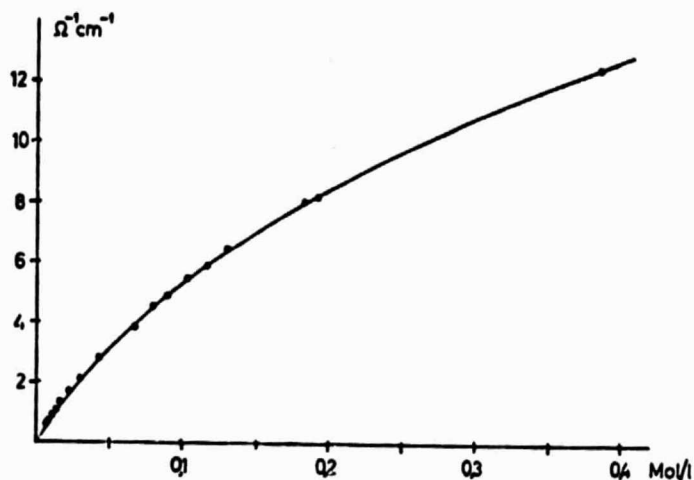


Fig. 4. Specific conductivity of NO_2PF_6 solutions in nitromethane at 25°C .

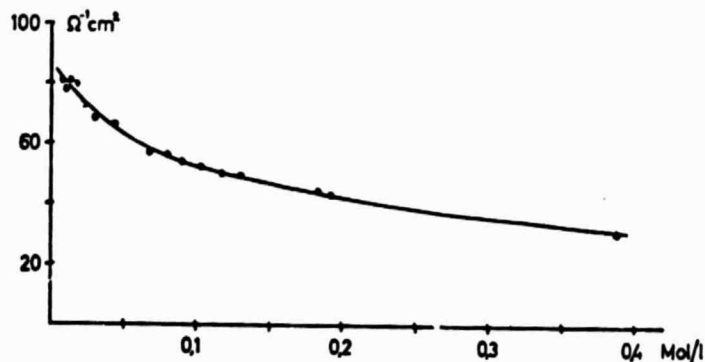


Fig. 5. Molar conductivity of NO_2PF_6 solutions in nitromethane at 25°C .

We hope later to be able to report in greater detail on this complex and the nitration mechanism of durene and other alkylic benzols.

4. Nitration of Durene by Means of an Acid Mixture in Organic Solvents

4.1 Mononitration of Durene

Since Smith et al. [6] as well as G. & M.P. Illuminati [5] performed nitrations by means of nitric acid, dissolved in a mixture of sulfuric acid and chloroform in a heterogeneous phase, we preferred to use nitromethane and acetonitrile as solvents, because, then, a homogeneous system with mixed acids could also be achieved. The reaction products were identified gaschromatologically (Table 4) in the same manner as mentioned above. It was found that under such conditions MND developed in part in large amounts; DND could not be identified in any of the tests made. On the other hand, 2,3,5,6,2',4',5'-heptamethyl-diphenylmethane and, especially, wide-chain reaction products developed in considerable amounts. We will discuss the latter in section 4.2. /1544

TABLE 4. DURENE NITRATION BY MEANS OF MIXED ACIDS IN ORGANIC SOLVENTS

Test No.	Solvent	Conc. of educts (mol/l)			Temp. °C	Reaction time (min)	Products (mol%) ¹			
		durene	HNO ₃	H ₂ SO ₄			durene	MND	HDM	others
8	CH ₃ NO ₂	0.011	0.011	0.022	1.0±0.5	120	15.5	45.2	12.0	27.3
9	CH ₃ NO ₂	0.054	0.054	0.108	1.0±0.5	150	8.7	60.7	6.8	23.8
10	CH ₃ NO ₂	0.104	0.106	0.212	1.0±0.5	130	3.0	83.6	5.6	7.8
11	CH ₃ NO ₂	0.109	0.109	0.327	1.0±0.5	60	4.2	45.0	4.9	45.9
12	CH ₃ NO ₂	0.100	0.100	0.200	25.0±0.5	10	-	76.2	-	23.8
13	CH ₃ NO ₂	0.200	0.200	0.200	35 ±2	10	-	51.9	-	48.1
14	CH ₃ CN	0.020	0.020	0.040	25.0±0.5	62	56.9	4.2	-	38.9
15	CH ₃ CN	0.100	0.100	0.200	25.0±0.5	60	20.0	6.3	-	73.7
16	CH ₃ CN	0.200	0.200	0.400	25.0±0.5	60	2.8	7.6	-	89.6

¹ HDM = 2,3,5,6,2',4',5'-heptamethyl-diphenylmethane. Other products: During tests nos. 14-16 (in CH₃CN) mainly N-acetyl-2,4,5-trimethylbenzylamine and some O-acetyl-2,4,5-trimethylbenzyl alcohol (cf. section 4,2). Concerning the time-dependency of the products during tests nos 8-10, see Figs. 6-8.

In Figs. 6 - 8 the change in concentration of educt and products, resulting from the mixed-acid nitration in relation to various concentrations of educt and a constant relationship between durene : HNO₃ : H₂SO₄ = 1 : 1 : 2 is illustrated as a function of the reaction time. It is obvious that, in this case, the above-mentioned S-shaped time-dependency is lost in relation to increasing concentration of educts.

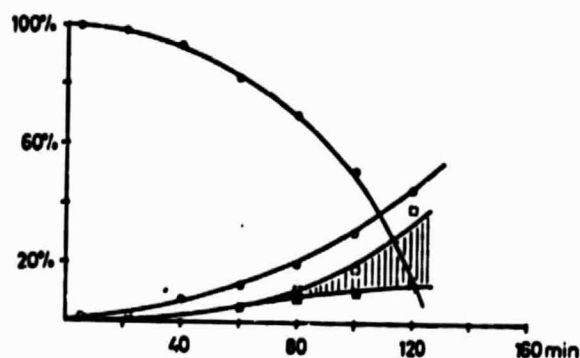


Fig. 6. Nitration of durene by means of an acid mixture in nitromethane at $1.0^{\circ} \pm 0.5^{\circ}\text{C}$.

- durene
- MND
- ▨ total by-products (hatched area = unknown by-products)
- heptamethyl-diphenylmethane

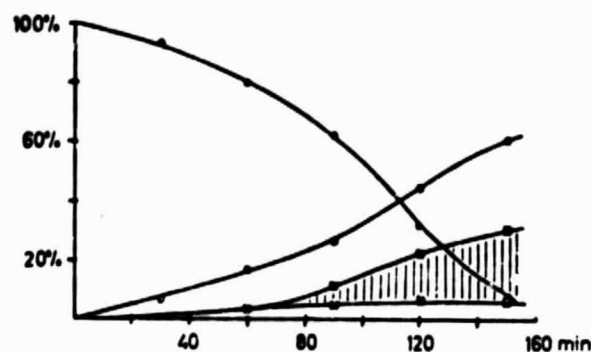


Fig. 7. Nitration similar to that in Fig. 6, however, at a concentration of durene $[D]_0 = 0.054 \text{ mol/l}$.

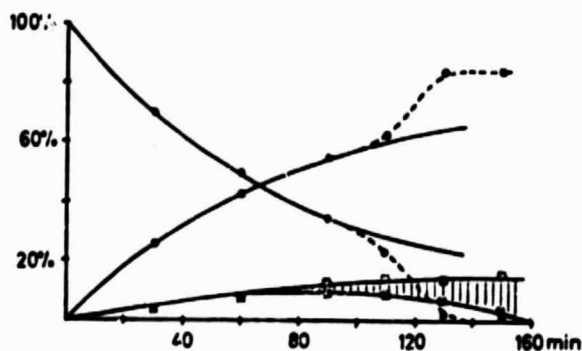


Fig. 8. Nitration similar to that in Fig. 6, however, at a concentration of durene $[D]_0 = 0.104 \text{ mol/l}$.

It can be seen from the results in Table 4 that in nitromethane MND is the main product, that no DND could be identified but that considerably more by-products develop than when using nitrylic salts and water in nitromethane. The amount of these by-products increases strongly in acetonitrile; there, only a few percents of MND could be identified and, again, no DND at all.

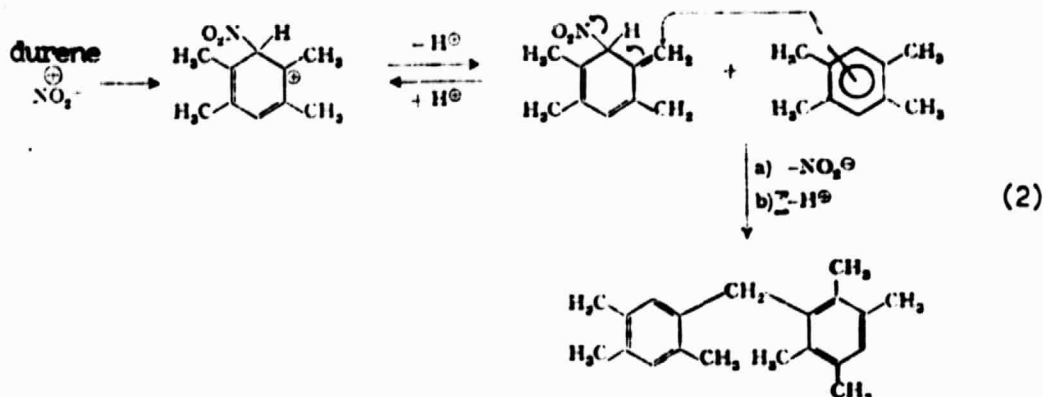
Although, - thanks to the classical investigations made by Ingold [13], - the existency of nitryl ions in solutions of nitric acid in nitromethane has been confirmed, we must leave the question open whether under our conditions as well (i.e., a system of $\text{HNO}_3/\text{H}_2\text{SO}_4/\text{CH}_3\text{NO}_2$), the nitrylic ion functions as an electrophilic particle.

4.2 Formation of By-products

Already Servis and Fields [14] were able to establish the fact that during /1545 nitration of toluol by means of nitric acid, methyl-diphenylmethane developed

in the form of a by-product. They assumed therefore that a hydrid-ion-mediated transmission of toluol unto the nitrylic ion took place under formation of nitric acid in the form of a separate stage of the reaction. The benzyl cation arising thereby should, then, substitute toluol electrophilically during a second stage, determining the speed of the reaction.

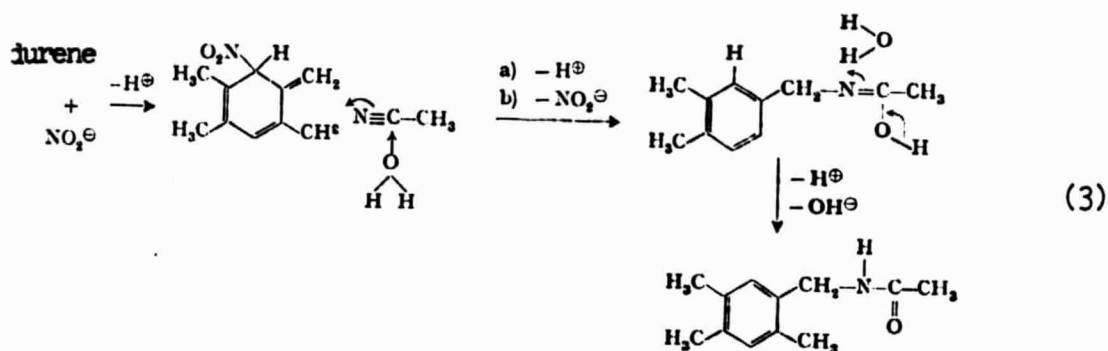
The 2.3.5.6.2'.4'.5'-heptamethyl-diphenylmethane, found by us during the nitration of durene, corresponds to the reaction observed by Servis and Fields [14]. We would like to deduce the following sequence (2) as a further reaction-mechnistic possibility based on the primary σ -complex, developed from the nitration of the nucleus. Although we have no experimental evidence for this, it seems very likely to us that there is no hydrid-mediated transmission during that reaction.



When using acetonitrile as solvent, the reaction with the solvent under formation of diphenyl-methane (2) occurs according to rank. The formation of N-acetyl-2.4.5-trimethyl-benzylamine can be traced to this phenomenon. Since acetonitrile under conditions of nitration with mixed acids to a certain extent can be hydrolyzed into acetic acid, some O-acetyl-2.4.5-trimethyl-benzyl alcohol will as well develop.

The formation of these products can be understood both according to the mechanism via the benzyl cation, suggested by Servis and Fields [14], as well as , analogically, according to mechanism (2) on the basis of the σ -complex, formed during the nitration of durene (3).

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5. Nitration of Durene by Means of Nitric Acid in Organic Solvents

Our experiments with nitromethane are contrary to a patent, recently published [15], according to which durene can be mononitrated with a satisfactory yield by means of nitric acid on acetonitrile or nitromethane.

We tried to reproduce the method described in this patent and to work out the products gaschromatographically in the manner described above. It is evident from Table 5 that practically no DND was formed, but the yield of MND was, in spite of that, extremely limited. It seems, in analogy with our experiments according to Table 4 that also under these conditions nitromethane is a somewhat more efficient solvent than acetonitrile for the mononitration of durene.

TABLE 5. NITRATION OF DURENE BY MEANS OF NITRIC ACID IN ORGANIC SOLVENTS ACCORDING TO WRIGHT [15].

Test No.	Solvent	Conc. of educt (mol/l)		Reaction time (min)	Products (mol%)		
		durene	HNO_3		durene	MND	by-products
17	CH_3CN	0.667	0.724	30	38.6	4.1	57.3
18	CH_3NO_2	0.667	0.724	30	11.2	12.1	76.7

We are obliged to the Swiss Board of Education and the University of Missouri, Rolla, MO, as well as to the CIBA Co., the J.R. Geigy Co., and the Sandoz Co., Basel, Switzerland, which allowed S.B. Hanna to participate in

this work, and to the Dainippon Ink, Co. Inc. as well as the three companies in Basel, mentioned above, which financially supported the stay of T. Saito at the Swiss Federal Technical University.

Experimental Part

1. Initial Products.

Durene was purified from the merchantile product by recrystallization: Melting point, $79^{\circ} - 80^{\circ}\text{C}$; purity (gas-chr.), 99.8%.

Nitromethane and acetonitrile were distilled over P_2O_5 (boiling point, $100.5^{\circ} - 101.0^{\circ}\text{C}$ and $80.5^{\circ} - 81.0^{\circ}\text{C}$, respectively). NO_2PF_6 : the merchantile product from Ozark-Mahonig Co., Oklahoma, was vacuum-desiccated in the presence of P_2O_5 . HNO_3 : concentrated nitric acid, 100% ($d = 1.52$) for analytical purposes (from the Merck Co.). H_2SO_4 : 98% sulfuric acid ($d = 1.84$) "for the determination of nitrogen" (from the Merck Co.).

2. Nitration of NO_2PF_6 in Nitromethane

2.1 Nitration in an Agitator Flask (Experiment no. 1)

A solution of 0.4865 g of NO_2PF_6 in 25 ml nitromethane were added, while stirring, to a solution of 0.3422 g durene in 50 ml nitromethane. The temperature was kept at $30^{\circ} \pm 1^{\circ}\text{C}$ by means of a thermostatic water bath. The agitator flask was enclosed in a tightfitting sleeve, preventing moisture from entering. After 45 min, 5 ml of the reacting solution was withdrawn in a pipette and ca. 5 ml water were added. To the aqueous solution, 0.0152 g naphthalin were added. The organic layer was dissociated and desiccated over a molecular sieve. A Varian Aerograph 1520 B with a 5% silicone SE 52 (phenyl) charged column at 210°C served for the gaschromatography. The identification of the products followed in the conventional manner by means of comparative compounds. The naphthalin added served as standard.

2.2 Nitration in a Mixed System According to Gordon & Wahl [10].

We used the apparatus constructed by Gordon & Wahl. Equal volumes of durene and NO_2PF_6 in nitromethane were forced from the storage vessels under

nitrogen pressure into a 3-way valve, functioning as mixer. From there it was conducted into water, which halted the reaction. Between the 3-way valve and the water, variously long capillary tubes (diameter, 0.5 mm) could be inserted via ball-and-socket joints in order to attain the reaction times desired. At a nitrogen pressure of 0.5 kp/cm^2 , the flow rate amounted to 10 ml/10 s. The processing and analysis of the reaction mixture was done in the manner described above. Results: see Table 6 or Fig. 1.

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TABLE 6. NITRATION OF DURENE IN A MIXED SYSTEM ACCORDING TO GORDON & WAHLE [10] AND IN AN AGITATOR FLASK

Test no.	19	20	21	22	23	24	cont.
Conc. of educt (mol/l) ¹	0.0060	0.0066	0.0116	0.0182	0.0406	0.0769	
Mixed system [DND]/[MND] _t	0.20	0.35	0.87	0.64	1.11	2.07	
acc. to reaction time (t) _s [10]	0.71	0.71	0.71	0.71	0.71	0.71	
Agita- [DND]/[MND] _t	0.74	0.72	2.63	-	2.26	4.68	
tor flask reaction time (t) _s	15	30	15	-	30	90	
cont. Test no.	25	26	27				
Conc. of educt (mol/l) ¹	0.1560	0.3119	0.3370				
Mixed system [DND]/[MND] _t	2.91	3.30	-				
acc. to reaction time (t) _s [10]	0.71	0.71	0.71				
Agita- [DND]/[MND] _t	6.35	-	9.4				
tor flask reaction time (t) _s	15	-	240				

3. Nitration of Durene by Means of NO_2PF_6 and Water in Nitromethane and Acetonitrile

Experiments 4 and 5: While stirring solutions of 0.0106 mol/l NO_2PF_6 and 0.0212 mol/l H_2O (experiment 4) or 0.078 mol/l NO_2PF_6 and 0.140 mol/l H_2O in 25 ml nitromethane were added to a solution of 0.0106 mol/l or 0.078 mol/l of durene in 25 ml nitromethane in an agitator flask while excluding

the entrance of any moisture (i.e., by means of a tightfitting sleeve). Processing and analyses were made as described above.

Experiments nos. 6 and 7 were similarly executed. For experiment no 6 an almost saturated solution was used. Since acetonitrile and water can be freely mixed, only about 1/5th of the volume of organic solution was added to the water and the entire mixture was analyzed gaschromatographically. The UV spectra (experiment no. 7) were executed by means of a 0.1 cm Quarts cell in a Cary 11 Spectrophotometer at 20°C.

4. Nitration by Means of Acid Mixtures

Ten ml of a solution of mixed acids at the concentrations mentioned in both of the corresponding solvents were added to the solutions of the amounts of durene, mentioned in Table 4, in 50 ml nitromethane or acetonitrile, respectively, in an agitator flask and processed and analyzed as mentioned above.

5. Isolation and Identification of the By-products

5.1 Nitration in Nitromethane

The reaction mixtures were eluted with petroleum ether (boiling point, 60 - 90°) in a neutral aluminium column. Initially durene, thereafter 2.3.5.6.2'.4'.5'-heptamethyl-diphenylmethane, then MND and, finally, DND appeared in the eluate. Other by-products could not be extracted by means of ethanol and chloroform.

Identification of 2.3.5.6.2'.4'.5'-heptamethyl-diphenylmethane: Boiling point, 144.6 - 145.2°C. MG = 266 (mass spectrum) IR spectrum (in chloroform): no nitro-band; very similar to the durene and the pentamethylbenzol spectra. NMR spectrum in CCl₄ (integrated signals within brackets): aromatic protons: δ = 6.18 (1) and 6.89 (2); aliphatic protons: δ = 2.03 (9), 2.15 (3), 2.25 (6), 2.34 (3) and 3.82 (2).

5.2 Nitration in Acetonitrile

The reaction products were separated by means of preparative thin-layer chromatography (prepared PSC-F 254 kieselgel plates from Merck, 20 x 20 cm, 2 mm thick). A 2:1 volume benzol/chloroform mixture served as eluant. The

fraction with the highest Rf value consisted of durene and MND, the second fraction of O-acetyl-2.4.5-trimethyl-benzyl alcohol and the final fraction of N-acetyl-2.4.5-trimethyl-benzamine.

Identification of O-acetyl-2.4.5-trimethyl-benzyl alcohol: Boiling point 87.0 - 88.0°C. MG = 192 (mass spectrum). IR spectrum (in KBr): very strong absorption at 1735 cm^{-1} . NMR spectrum (in CDCl_3 ; relative intensity in brackets): aromatic protons, $\delta = 6.03$ (1) and 7.02 (1); aliphatic protons, $\delta = 2.19$ (6), 2.34 (3), 2.87 (3) and 4.93 (2).

Identification of N-acetyl-2.4.5-trimethyl-benzylamine: Boiling point: /1548 140 - 141°C. MG = 192 (mass spectrum). IR spectrum (in KBr): strong signal at 1650 cm^{-1} . NMR spectrum (in CDCl_3): aromatic protons: $\delta = 1.97$ (3), 2.23 (9), 4.33 and 4.42 (doublet, 2).

6. Nitration of Durene by Means of Nitric Acid in Organic Solvents According to [15].

Experiment no. 17: At 40°C and while stirring 1.80 ml of HNO_3 (100%, $d = 1.52$) solution were added to a solution of 5.374 g durene in 50 ml. acetonitrile. This solution was boiled during reflux for 30 min and, subsequently, emptied into 100 ml water. After addition of naphthalin (similarly as in the other experiments), the mixture was extracted with ether and the ether fraction analyzed gaschromatographically like above.

The experiment in nitromethane (no 18) was executed in a similar manner. During the processing, the organic layer was, however, separated, desiccated over a molecular sieve and analyzed as usually.

7. Measurements of Conductivity

The measurements were made by means of a Philips PR 9501 conductometer at a measuring frequency of 80 c/s. The change in conductivity was transferred via the instrument in the form of a voltage change to the recorder, a Hitachi QD 53. As measuring cells, test tubes (10 ml), closed by a ground tap, were used, into which the measuring electrodes could be dipped. The latter had a 0.5 cellular constant. The cells were heated to $25 \pm 0.5^\circ\text{C}$ by means of a Colora thermostat.

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